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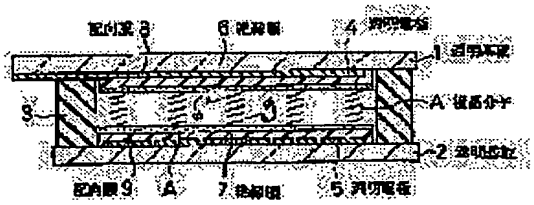
(54) LIQUID CRYSTAL DISPLAY ELEMENT AND FORMATION OF ITS ORIENTED FILM

(57)Abstract:

PURPOSE: To provide the liquid crystal display device which is free from a defect in initial orientation of a liquid crystal and a defect in reverse tilt discrimination orientation at the time of impression of a driving voltage and has good display quality by orienting liquid crystal molecules by providing these molecules with a desired pretilt angle as the liquid crystal display element formed with horizontally oriented films consisting of polyimide by an LB method.



CONSTITUTION: The horizontally oriented films 8, 9 consisting of polyimide films formed by laminating monomolecular films of compds. constituted by bringing polyamic acid and long chain alkyl amine into reaction by the LB method and subjecting the laminated films to an imidization treatment are so formed by controlling the mixing ratio of the polyamic acid and the long chain alkyl amine that the long chain alkyl groups per unit area remain at a prescribed ratio. The liquid crystal molecules A are oriented at the pretilt angle ϕ meeting the remaining ratio of the long chain alkyl groups per unit areas of the horizontally oriented films 8, 9.

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CLAIMS

[Claim(s)]
[Claim 1] To the field which counters mutually [the transparence substrate of the couple which counters on both sides of a liquid crystal layer], a transparent electrode, It is the liquid crystal display component in which the level orientation film which consists of polyimide film which carried out the laminating of the monomolecular film of the compound to which the amine which has polyamic acid and a long-chain alkyl group by the Langmuir-Blodgett's technique is made to come to react, and imide--ization-processed this cascade screen was formed. Said level orientation film It is formed so that the mixing ratio of said polyamic acid and the amine which has a long-chain alkyl group may be controlled and said long-chain alkyl group may remain at a predetermined rate to per unit area. The liquid crystal display component characterized by the liquid crystal molecule carrying out orientation with the pre tilt angle according to the long-chain alkyl group residual rate per unit area of said level orientation film.
[Claim 2] The predetermined number laminating of the monomolecular film of the compound to which the amine which has polyamic acid and a long-chain alkyl group by the Langmuir-Blodgett's technique on the transparence substrate in which the transparent electrode was formed is made to come to react is carried out. It is the approach of forming the level orientation film which imide--ization-processes this cascade screen on condition that predetermined, and consists of polyimide film. The formation approach of the orientation film characterized by obtaining the level orientation film which consists of polyimide film which the mixing ratio of said polyamic acid and the amine which has a long-chain alkyl group was controlled [film], and made said long-chain alkyl group remain at a predetermined rate to per unit area.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the formation approach of the liquid crystal display component to which orientation of the liquid crystal molecule was carried out horizontally, and its level orientation film.
[0002]
[Description of the Prior Art] There are some which used the thing in TN (Twisted Nematic) mode, the thing in STN (super twisted nematic) mode, the thing of the level orientation mold of the ECB (electric-field control mold birefringence) modes, a ferroelectric liquid crystal, or antiferroelectricity liquid crystal in the liquid crystal display component to which orientation of the liquid crystal molecule was carried out horizontally.
[0003] These liquid crystal display components have the composition in which a transparent electrode and the level orientation film for carrying out orientation of the liquid crystal molecule horizontally were formed to the field which counters mutually [the transparence substrate of the couple which counters on both sides of a liquid crystal layer].
[0004] although the level orientation film prepared on the substrate of these liquid crystal devices was conventionally formed by the approach of applying polyimide etc. on a substrate and carrying out rubbing processing of the film surface, or the approach of carrying out the method vacuum evaporationo of the oxidation silicon (Si O2) etc. of slanting on a substrate — recently — Langmuir BUROJIETTO (Langumuir-Blodgett) — the approach of forming the level orientation film which consists of polyimide film by law is adopted increasingly.
[0005] The above-mentioned Langmuir-Blodgett's technique (it is hereafter described as the LB method) The substrate which made the monomolecular film and was made beforehand immersed at right angles to underwater on a potentiometric surface with constant speed with a pull-up Are the approach of making the monomolecular film on the water surface putting on a substrate, and formation of the polyimide film by this LB method The amine which has polyamic acid and a long-chain alkyl group (hereafter) Carry out the multiple-times loop of the process made to put on a substrate by law, and the laminating of said monomolecular film is carried out on a substrate. long-chain alkylamine — saying — the monomolecular film of the polyamic acid derivative compound (polyamic acid salt) which comes to carry out an ionic bond reaction — LB — It is carried out by the approach of imide--ization-processing this cascade screen and using as the polyimide film.
[0006] Above LB — the stacking tendency the polyimide film with which the monomolecular film of the polyamic acid derivative compound put by law on the substrate imide-ized the cascade screen of this monomolecular film since the long molecule of molecule length was located in a line along the pull-up direction of a substrate makes [stacking tendency] an one direction carry out [stacking tendency] orientation of the liquid crystal molecule to homogeneity — **** — this polyimide film can be used as the level orientation film as it is, without getting down, therefore carrying out rubbing processing of that film surface.
[0007] By the way, in a liquid crystal display component, since the orientation condition of a liquid

crystal molecule influences greatly the electro-optics property of a liquid crystal display component, in order to obtain a good display, it is necessary to improve stability of the orientation of a liquid crystal molecule.

[0008] The important element which influences the stability of the orientation of this liquid crystal molecule is the pre tilt angle (include angle which the major axis of a liquid crystal molecule makes to a substrate side) of the liquid crystal molecule given with the orientation film, and the stability of the orientation of a liquid crystal molecule becomes good, so that this pre tilt angle is large.

[0009]

[Problem(s) to be Solved by the Invention] However, orientation of the level orientation film formed by the describing [above] LB method is carried out in the condition (pre tilt angle of 0 degree) of not carrying out the pre tilt of the liquid crystal molecule.

[0010] For this reason, the conventional liquid crystal display component had the problem of having produced the poor initial orientation of liquid crystal, or generating poor reverse tilt discreenation orientation at the time of driver voltage impression.

[0011] This invention is united and aims at offering the formation approach of the level orientation film while it offers the liquid crystal display component of good display quality without the poor initial orientation of liquid crystal and the poor reverse tilt discreenation orientation at the time of driver voltage impression etc. to which orientation of the pre tilt angle of a request of a liquid crystal molecule was given and carried out as a liquid crystal display component in which the level orientation film which consists of polyimide by the LB method was formed.

[0012]

[Means for Solving the Problem] The liquid crystal display component of this invention to the field which counters mutually [the transparence substrate of the couple which counters on both sides of a liquid crystal layer] A transparent electrode, It comes to form the level orientation film which consists of polyimide film which carried out the laminating of the monomolecular film of the compound to which the amine which has polyamic acid and a long-chain alkyl group by the LB method is made to come to react, and imide-ization-processed this cascade screen. And said level orientation film is formed so that the mixing ratio of said polyamic acid and the amine which has a long-chain alkyl group may be controlled and said long-chain alkyl group may remain at a predetermined rate to per unit area. It is characterized by the liquid crystal molecule carrying out orientation with the pre tilt angle according to the long-chain alkyl group residual rate per unit area of said level orientation film.

[0013] The formation approach of the level orientation film of this invention moreover, on the transparence substrate in which the transparent electrode was formed The predetermined number laminating of the monomolecular film of the compound to which the amine which has polyamic acid and a long-chain alkyl group by the LB method is made to come to react is carried out. It is the approach of forming the level orientation film which imide-ization-processes this cascade screen on conditions to predetermined, and consists of polyimide film. The mixing ratio of said polyamic acid and the amine which has a long-chain alkyl group is controlled, and it is characterized by obtaining the level orientation film which consists of polyimide film which made said long-chain alkyl group remain at a predetermined rate to per unit area.

[0014]

[Function] namely, the liquid crystal display component of this invention — LB — the level orientation film which consists of polyimide film formed by law Since it forms so that the mixing ratio of polyamic acid and the amine which has a long-chain alkyl group may be controlled and a long-chain alkyl group may remain at a predetermined rate to per unit area, and said long-chain alkyl group has hydrophobicity, The surface tension of the orientation film becomes small and a liquid crystal molecule carries out level orientation with the pre tilt angle according to said surface tension, so that the residual rate of the long-chain alkyl group per unit area of the level orientation film is made [many].

[0015] For this reason, if the mixing ratio of said polyamic acid and the amine which has a long-chain alkyl group is controlled and the residual rate of the long-chain alkyl group per unit area of the above-

mentioned level orientation film is controlled, orientation of the pre tilt angle of a request of a liquid crystal molecule can be given and carried out, and good display quality without the poor initial orientation of liquid crystal and the poor reverse tilt discreenation orientation at the time of driver voltage impression can be acquired.

[0016] The laminating of the monomolecular film of the compound to which the amine which has polyamic acid and a long-chain alkyl group by law is made to come to react is carried out. moreover, the formation approach of the level orientation film of this invention — LB — It is what forms the polyimide film with which the cascade screen of this monomolecular film is imide—ization-processed, and long-chain alkylamine remains. By controlling the mixing ratio of said polyamic acid and the amine which has a long-chain alkyl group according to the number of laminatings and its imide-ized condition of the monomolecular film set up beforehand Since the long-chain alkyl group residual rate of said polyimide film is decided according to it, the level orientation film to which orientation of the pre tilt angle of a request of a liquid crystal molecule is given and carried out can be obtained.

[0017]

[Example] Hereafter, the example of this invention is explained with reference to a drawing.

[0018] Drawing 1 is the sectional view of a liquid crystal display component. This liquid crystal display component joins the transparence substrates 1 and 2 of a couple which consist of glass etc. through the frame-like sealant 3, it is what enclosed liquid crystal with both this substrate 1 and the field surrounded by the sealant 3 between two, and transparent electrodes 4 and 5 are formed in the field where both the substrates 1 and 2 counter mutually, respectively. Moreover, the electrode forming face of both these substrates 1 and 2 is covered by the transparent insulator layers 6 and 7 which consist of oxidation silicon (Si O2) etc., and the level orientation film 8 and 9 is formed on these insulator layers 6 and 7.

[0019] In addition, this liquid crystal display component is the thing in TN mode or STN mode, and both the substrates 1 and the molecule A of the liquid crystal enclosed among two are regulated by said orientation film 8 and 9, and are carrying out twist orientation of each orientation direction of the liquid crystal molecule A near both the substrates 1 and the orientation film 8 and 9 by the side of two on the predetermined twist square between both the substrates 1 and 2. However, at drawing 1 , the liquid crystal molecule A is shown in the condition of having not carried out twist orientation, for convenience.

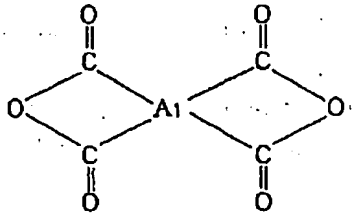
[0020] The above-mentioned level orientation film 8 and 9 consists of polyimide film which imide-ized the film which made the monomolecular film of the compound to which polyamic acid and the amine (henceforth long-chain alkylamine) which has a long-chain alkyl group are made to all come to react put on several layers – dozens of layers in piles.

[0021] These level orientation film 8 and 9 is formed by the following approaches. In addition, although formation of the level orientation film 8 prepared in one substrate 1 is explained, the level orientation film 9 prepared in the substrate 2 of another side is formed similarly here.

[0022] The above-mentioned polyamic acid is expressed with the structure expression of the following [-izing 3], and this polyamic acid compounds the tetracarboxylic dianhydride expressed with the structure expression of [-izing 1], and the diamine expressed with the structure expression of [-izing 2], and is obtained.

[0023]

[Formula 1]

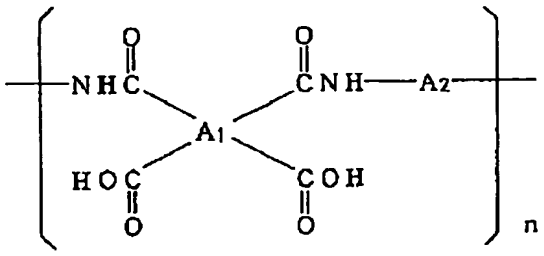


[0024]

[Formula 2]

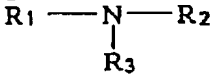
$H_2N—A_2—NH_2$

[0025]
[Formula 3]



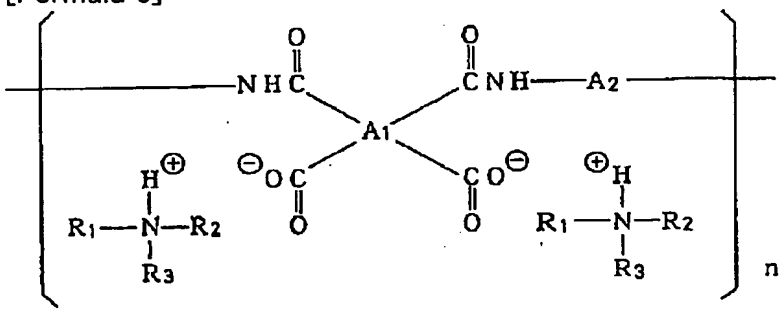
nは1以上の整数

[0026] Moreover, the above-mentioned long-chain alkylamine is for giving hydrophobicity to polyamic acid with a hydrophilic property, and this long-chain alkylamine is expressed with the structure expression of the next [-izing 4].
[0027]
[Formula 4]



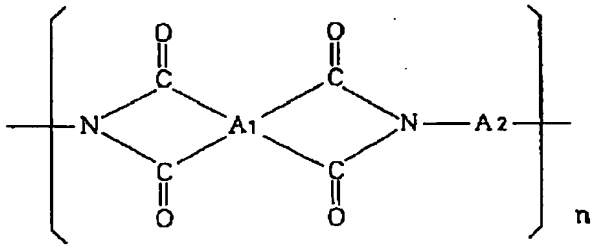
R1 , R2 は低級アルキル基または水素原子
R3 は長鎖のアルキル基

[0028] The solution which melted the above-mentioned polyamic acid to the solvent, and the solution which melted the above-mentioned long-chain alkylamine to the same solvent are mixed at a predetermined rate, the ionic bond reaction of polyamic acid and the long-chain alkylamine is carried out, and the solution of the polyamic acid derivative compound (polyamic acid salt) expressed with the structure expression of the following [-izing 5] is created. In addition, as a solvent of the above-mentioned polyamic acid and long-chain alkylamine, the mixed solvent which mixed NMP (N-methyl-2-pyrrolidinone) and benzene at a rate of 1:1 is used.
[0029]
[Formula 5]



[0030] and the substrate 1 top which the above-mentioned level orientation film 8 formed the transparent electrode 4, and formed the insulator layer 6 on it — LB — the laminating of the monomolecular film of the above-mentioned polyamic acid derivative compound is carried out to a predetermined layer by law, and it is formed by heat-treating the cascade screen of this monomolecular film. drawing 2 — a substrate 1 top — the monomolecular film of a polyamic acid derivative compound — — LB — how to make it covering by law is shown. Covering of this monomolecular film is performed as follows. First, hydrophilic processing is performed to the monomolecular-film covering side (the 6th page of insulator layer) of the above-mentioned substrate 1, and this substrate 1 is made immersed at right

angles to underwater [in a cistern 10].
[0031] Next, the solution of the above-mentioned polyamic acid derivative compound is dropped on the water surface between the migration barrier 11 of the shape of a bar prepared in water surface height, and a substrate 1, and the monomolecular film a is developed on the water surface.
[0032] Next, moving the migration barrier 11 in the direction of a substrate with constant speed (2 mm/min), and pushing a monomolecular film a in the direction of a substrate, after moving the migration barrier 11 in the direction of a substrate, clustering the single molecule on the water surface and adjusting the surface pressure of a monomolecular film a to 1 constant pressure (25 dyn/cm), it is made to align with this, a substrate 1 is pulled up, and the monomolecular film a on the water surface is made to put on a substrate 1.
[0033] Since a part with a hydrophilic property adheres to the substrate 1 which has performed hydrophilic processing and the single molecule on the water surface can be pulled up at this time, a molecule puts a monomolecular film a on a substrate 1 in the condition of having stood in a line in the about 1 direction. The following repeats the covering process of the above-mentioned monomolecular film a, and carries out the laminating of the above-mentioned monomolecular film a to a predetermined layer on a substrate 1.
[0034] Thus, after carrying out the laminating of the monomolecular film a of a polyamic acid derivative compound on a substrate 1, heat treatment heated above 200 degrees C for about 1 hour is performed. The level orientation film 8 on which imide-ization of the cascade screen on a substrate 1 progresses to, and alkylamine remains by this heat treatment is formed.
[0035] In this case, while that alkylamine is removed, the dehydration ring closure of the single molecule cascade screen of the polyamic acid derivative compound which is a compound in which polyamic acid and long-chain alkylamine carried out ionic bond is carried out, and although it is imide-ized so that it may become polyimide with structure like the next [-izing 6], alkylamine remains at a predetermined rate, without completing that imide-ization. The amount of residuals of this alkylamine changes with the mixing ratios of polyamic acid and long-chain alkylamine, when heat treatment conditions etc. are fixed. Therefore, the residual rate of a long-chain alkyl group is controllable by setting up suitably the mixing ratio of polyamic acid and long-chain alkylamine.
[0036]
[Formula 6]



[0037] In the above-mentioned liquid crystal display component, the level orientation film 8 and 9 which consists of polyimide film of both the substrates 1 and 2 and by setting up suitably the mixing ratio of polyamic acid and long-chain alkylamine Long-chain alkyl group R3 in the long-chain alkylamine shown in the above per that unit area [-izing 4] A residual rate is controlled, it is formed and orientation of the liquid crystal molecule A is carried out with desired pre tilt angle phi with these level orientation film 8 and 9.
[0038] drawing 3 and drawing 4 — the mixing ratio of polyamic acid and long-chain alkylamine — controlling — LB — long-chain alkyl group R3 of the level orientation film 8 and 9 which consists of polyimide film formed by law It is drawing showing a residual condition typically, and a long-chain alkyl group residual condition when drawing 3 makes the amount (molar quantity) of polyamic acid and long-chain alkylamine almost the same, and drawing 4 show the long-chain alkyl group residual condition when making [more] the amount of long-chain alkylamine than the amount of polyamic acid.
[0039] this drawing 3 and drawing 4 — like — Above LB — long-chain alkyl group R3 of the level

orientation film 8 and 9 which consists of polyimide film formed by law, so that a residual rate changes with the mixing ratios of polyamic acid and long-chain alkylamine and the amount of long-chain alkylamine is made [many] -- long-chain alkyl group R3 That distribution also becomes homogeneity while a residual rate increases.

[0040] and the above-mentioned liquid crystal display component -- setting -- LB -- the level orientation film 8 and 9 which consists of polyimide film formed by law -- per the unit area -- long-chain alkyl group R3 Since the mixing ratio of polyamic acid and long-chain alkylamine is controlled and formed so that it may remain at a predetermined rate, orientation of pre tilt angle phi of a request of a liquid crystal molecule can be given and carried out.

[0041] this -- the above-mentioned long-chain alkyl group -- hydrophobicity -- **** -- since it is -- it is -- long-chain alkyl group R3 per unit area of the level orientation film 8 and 9 The surface tension of the orientation film 8 and 9 becomes small, and the liquid crystal molecule A carries out orientation with pre tilt angle phi, so that a residual rate is made [many].

[0042] For this reason, the mixing ratio of the above-mentioned polyamic acid and long-chain alkylamine is controlled, and it is the long-chain alkyl group R3 per unit area of the level orientation film 8 and 9. If a residual rate is controlled, orientation of the pre tilt angle of a request of the liquid crystal molecule A can be given and carried out, and good display quality without the poor initial orientation of liquid crystal and the poor reverse tilt discreenation orientation at the time of driver voltage impression can be acquired.

[0043] LB to which the above level orientation film 8 and 9 of a long-chain alkyl group residual rate mentioned above the mixing ratio of polyamic acid and long-chain alkylamine -- it controls and forms according to the number of laminatings and its imide-ized condition of the monomolecular film a which carries out a laminating by law.

[0044] Namely, the formation approach of these level orientation film 8 and 9 In case the laminating of the monomolecular film a of the compound to which polyamic acid and long-chain alkylamine are made to come to react by the LB method is carried out, by controlling the mixing ratio of said polyamic acid and long-chain alkylamine Long-chain alkyl group R3 in the polyimide film which processes the cascade screen of said monomolecular film a imide-ization, and forms it It is what controls a residual rate. If the mixing ratio of said polyamic acid and long-chain alkylamine is controlled according to the number of laminatings and its imide-ized condition of a monomolecular film a, since the long-chain alkyl group residual rate per unit area will be decided according to it, The level orientation film 8 and 9 to which orientation of pre tilt angle phi of a request of the liquid crystal molecule A is given and carried out can be obtained.

[0045] Drawing 5 shows the relation between the mixing ratio of the above-mentioned polyamic acid and long-chain alkylamine, the number of laminatings of the above-mentioned monomolecular film a, imide-ized temperature, and the surface tension of the formed orientation film, chooses the mixing ratio (mole ratio) of polyamic acid and long-chain alkylamine as two kinds of polyamic acid:long-chain alkylamine =1:3 and polyamic acid:long-chain alkylamine =1:5, and shows the example which imide--ization-processed each at the imide-ized temperature of 200 degrees C here.

[0046] The orientation film which consists of polyimide film which formed by setting the mixing ratio of polyamic acid and long-chain alkylamine to 1:3 like this drawing 5 When the number of laminatings of a monomolecular film a is about 18 or less layers, surface tension is too large and the pre tilt of the liquid crystal molecule A is hardly carried out (pre tilt angle phi= 0). When the number of laminatings of a monomolecular film a is made [more] than it, it becomes the surface tension to which it has the liquid crystal molecule A, and orientation of a certain amount of pre tilt angle phi (it is phi= 3.2 degrees by the case where for example, the number of laminatings is 23 layers) is carried out. In addition, this surface tension becomes so small that the number of laminatings of a monomolecular film a is made [many], and pre tilt angle phi of the liquid crystal molecule A becomes large in connection with it.

[0047] Moreover, when the number of laminatings of a monomolecular film a is about ten or less layers, surface tension is too large, the liquid crystal molecule A hardly carries out a pre tilt, but the orientation

film which consists of polyimide film which formed by setting the mixing ratio of polyamic acid and long-chain alkylamine to 1:5 will become the surface tension in which the liquid crystal molecule A carries out orientation with pre tilt angle phi, if the number of laminatings of a monomolecular film a is made [more] than it. Pre tilt angle phi in this case is phi= 13 degrees or more in the case where phi= 0.4 degrees and the number of laminatings are about 17 or more layers in the case where for example, the number of laminatings is about 11 layers. In addition, although it becomes so small that the surface tension of the orientation film makes [many] the number of laminatings of a monomolecular film a also in this case and pre tilt angle phi of the liquid crystal molecule A becomes large in connection with it, if the number of laminatings exceeds about 22 layers, pre tilt angle phi will become close to 90 degrees, and the liquid crystal molecule A will carry out vertical orientation.

[0048] In addition, even if the amount of the long-chain alkylamine to polyamic acid is below 3 times (mixing ratio 1:3), the liquid crystal molecule A can carry out pre tilt orientation by making [more / still] the number of laminatings of a monomolecular film a, but if the number of laminatings of a monomolecular film a is made [many], the orientation film 8 and 9 will become thick and applied voltage will descend greatly in the orientation film.

[0049] Therefore, as for the mixing ratio of the above-mentioned polyamic acid and long-chain alkylamine, it is desirable to consider as the range of polyamic acid:long-chain alkylamine =1:3-1:5, and it can obtain the level orientation film 8 and 9 to which orientation of pre tilt angle phi of a request of the liquid crystal molecule A is given and carried out, without making [many / not much] the number of laminatings of a monomolecular film a, if it is this range.

[0050] In addition, although heat treatment is performing imide-ized processing of the cascade screen of a monomolecular film a in the above-mentioned example This imide-ized processing also by the chemical treatment by solutions, such as an acid anhydride Moreover, if you may carry out by using together both said chemical treatments and above-mentioned heat treatments and the mixing ratio of polyamic acid and long-chain alkylamine is controlled also in that case according to the number of laminatings and its imide-ized condition of a monomolecular film a The level orientation film to which orientation of the pre tilt angle of a request of a liquid crystal molecule is given and carried out can be obtained.

[0051] Moreover, although the liquid crystal display component of the above-mentioned example is the thing in TN mode or STN mode, this invention is applicable to the liquid crystal display component of the level orientation mold of the ECB (electric-field control mold birefringence) modes, the liquid crystal display component which used a ferroelectric liquid crystal or antiferroelectricity liquid crystal.

[0052]

[Effect of the Invention] the liquid crystal display component of this invention -- LB -- since the level orientation film which consists of polyimide film formed by law is formed so that the mixing ratio of polyamic acid and long-chain alkylamine may be controlled and a long-chain alkyl group may remain at a predetermined rate to per unit area, the pre tilt angle of a request of a liquid crystal molecule is given, orientation can be carried out, and good display quality without the poor initial orientation of liquid crystal and the poor reverse tilt discreenation orientation at the time of driver voltage impression can be acquired.

[0053] The laminating of the monomolecular film of the compound to which polyamic acid and long-chain alkylamine are made to come to react by law is carried out. moreover, the formation approach of the level orientation film of this invention -- LB -- By the approach of forming the polyimide film with which this cascade screen is imide-ized and a long-chain alkyl group remains Since it is what controls the residual rate of the long-chain alkyl group of said polyimide film by controlling the mixing ratio of said polyamic acid and long-chain alkylamine according to the number of laminatings and its imide-ized condition of the monomolecular film set up beforehand, The level orientation film to which orientation of the pre tilt angle of a request of a liquid crystal molecule is given and carried out can be obtained.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The sectional view of a liquid crystal display component showing one example of this invention.
[Drawing 2] Drawing showing the laminated layers method of the monomolecular film to the substrate top by the LB method.
[Drawing 3] Long-chain alkyl group R3 of the level orientation film which made the amount of polyamic acid and long-chain alkylamine almost the same, and formed it Drawing showing a residual condition typically.
[Drawing 4] Long-chain alkyl group R3 of the level orientation film which made [many] the amount of long-chain alkylamine and formed it rather than the amount of polyamic acid Drawing showing a residual condition typically.
[Drawing 5] Drawing showing the relation between the mixing ratio of polyamic acid and long-chain alkylamine, the number of laminatings of a monomolecular film, imide-ized temperature, and the surface tension of the formed orientation film.
[Description of Notations]
1 2 — Substrate
4 5 — Electrode
6 7 — Insulator layer
8 9 — Level orientation film which consists of polyimide film formed by the LB method
A — Liquid crystal molecule

[Translation done.]

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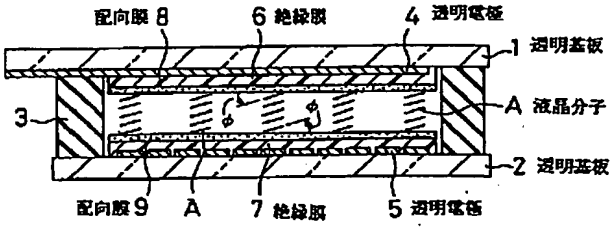
(54)【発明の名称】液晶表示素子およびその配向膜の形成方法

(57)【要約】

【目的】ＬＢ法によりポリイミドからなる水平配向膜を形成した液晶表示素子として、液晶分子を所望のプレチルト角をもたせて配向させた、液晶の初期配向不良や駆動電圧印加時のリバースチルトディスクリネーション配向不良等がない良好な表示品質の液晶表示素子を提供する。

【構成】ＬＢ法によりポリアミック酸と長鎖アルキルアミンとを反応させてなる化合物の単分子膜を積層しこの積層膜をイミド化処理して形成するポリイミド膜からなる水平配向膜８，９を、前記ポリアミック酸と長鎖アルキルアミンとの混合比を制御して単位面積当たりに長鎖アルキル基が所定の割合で残留するように形成し、液晶分子Ａを、前記水平配向膜８，９の単位面積当たりの長鎖アルキル基残留割合に応じたプレチルト角φで配向させた。



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【特許請求の範囲】

【請求項１】液晶層をはさんで対向する一対の透明基板の互いに対向する面に、透明電極と、ラングミュア・ブロジェット法によりポリアミック酸と長鎖アルキル基を有するアミンとを反応させてなる化合物の単分子膜を積層してこの積層膜をイミド化処理したポリイミド膜からなる水平配向膜とを形成した液晶表示素子であって、前記水平配向膜は、前記ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を制御して単位面積当たりに前記長鎖アルキル基が所定の割合で残留するように形成されており、液晶分子が、前記水平配向膜の単位面積当たりの長鎖アルキル基残留割合に応じたプレチルト角をもって配向していることを特徴とする液晶表示素子。

【請求項２】透明電極を形成した透明基板上に、ラングミュア・ブロジェット法によりポリアミック酸と長鎖アルキル基を有するアミンとを反応させてなる化合物の単分子膜を所定数積層し、この積層膜を所定の条件でイミド化処理してポリイミド膜からなる水平配向膜を形成する方法であって、

前記ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を制御し、単位面積当たりに前記長鎖アルキル基を所定の割合で残留させたポリイミド膜からなる水平配向膜を得ることを特徴とする配向膜の形成方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、液晶分子を水平方向に配向させた液晶表示素子およびその水平配向膜の形成方法に関するものである。

【０００２】

【従来の技術】液晶分子を水平方向に配向させた液晶表示素子には、ＴＮ（ツイステッド・ネマティック）モードのもの、ＳＴＮ（スーパー・ツイステッド・ネマティック）モードのもの、ＥＣＢ（電界制御型複屈折）モードのうちの水平配向型のもの、強誘電性液晶または反強誘電性液晶を用いたもの等がある。

【０００３】これらの液晶表示素子は、液晶層をはさんで対向する一対の透明基板の互いに対向する面に、透明電極と、液晶分子を水平方向に配向させるための水平配向膜とを形成した構成となっている。

【０００４】これらの液晶素子の基板上に設けられる水平配向膜は、従来、基板上にポリイミド等を塗布してその膜面をラビング処理する方法、または基板上に酸化硅素（SiO_2）等を斜方蒸着する方法によって形成されていたが、最近では、ラングミュア・ブロジェット（Langumuir-Blodgett）法によってポリイミド膜からなる水平配向膜を形成する方法が採用されるようになってきている。

【０００５】上記ラングミュア・ブロジェット法（以下、ＬＢ法と記す）は、静水面上に単分子膜を作り、あらかじめ水中に垂直に浸漬させておいた基板を一定速度で引上げながら、水面上の単分子膜を基板上に被着させてゆく方法であり、このＬＢ法によるポリイミド膜の形成は、ポリアミック酸と長鎖アルキル基を有するアミン（以下、長鎖アルキルアミンという）とをイオン結合反応させてなるポリアミック酸誘導体化合物（ポリアミック酸塩）の単分子膜をＬＢ法により基板上に被着させる工程を複数回繰返して前記単分子膜を基板上に積層し、この積層膜をイミド化処理してポリイミド膜とする方法で行なわれている。

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【０００６】上記ＬＢ法によって基板上に被着されたポリアミック酸誘導体化合物の単分子膜は、分子長の長い分子が基板の引上げ方向に沿って並んでいるため、この単分子膜の積層膜をイミド化したポリイミド膜は、液晶分子を一方向に均一に配向させる配向性をもっており、したがって、その膜面をラビング処理することなく、このポリイミド膜をそのまま水平配向膜とすることができる。

【０００７】ところで、液晶表示素子においては、液晶分子の配向状態が液晶表示素子の電気光学特性に大きく影響するため、良好な表示を得るには、液晶分子の配向の安定性を良くしてやる必要がある。

【０００８】この液晶分子の配向の安定性を左右する重要な要素は、配向膜によって与えられる液晶分子のプレチルト角（液晶分子の長軸が基板面に対してなす角度）であり、このプレチルト角が大きいほど、液晶分子の配向の安定性が良くなる。

【０００９】

【発明が解決しようとする課題】しかしながら、上記ＬＢ法により形成された水平配向膜は、液晶分子をプレチルトしない（プレチルト角０°）状態で配向させる。

【００１０】このため、従来の液晶表示素子は、液晶の初期配向不良を生じたり、駆動電圧印加時にリバースチルトディスクリネーション配向不良を発生したりするという問題をもっていた。

【００１１】本発明は、ＬＢ法によりポリイミドからなる水平配向膜を形成した液晶表示素子として、液晶分子を所望のプレチルト角をもたせて配向させた、液晶の初期配向不良や駆動電圧印加時のリバースチルトディスクリネーション配向不良等がない良好な表示品質の液晶表示素子を提供するとともに、あわせて、その水平配向膜の形成方法を提供することを目的としたものである。

【００１２】

【課題を解決するための手段】本発明の液晶表示素子は、液晶層をはさんで対向する一対の透明基板の互いに対向する面に、透明電極と、ＬＢ法によりポリアミック酸と長鎖アルキル基を有するアミンとを反応させてなる化合物の単分子膜を積層してこの積層膜をイミド化処理したポリイミド膜からなる水平配向膜とを形成してなり、かつ、前記水平配向膜は、前記ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を制御して単位

面積当たりに前記長鎖アルキル基が所定の割合で残留するように形成されており、液晶分子が、前記水平配向膜の単位面積当たりの長鎖アルキル基残留割合に応じたプレチルト角をもって配向していることを特徴とするものである。

【００１３】また、本発明の水平配向膜の形成方法は、透明電極を形成した透明基板上に、ＬＢ法によりポリアミック酸と長鎖アルキル基を有するアミンとを反応させてなる化合物の単分子膜を所定数積層し、この積層膜を所定に条件でイミド化処理してポリイミド膜からなる水平配向膜を形成する方法であって、前記ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を制御し、単位面積当たりに前記長鎖アルキル基を所定の割合で残留させたポリイミド膜からなる水平配向膜を得ることを特徴とするものである。

【００１４】

【作用】すなわち、本発明の液晶表示素子は、ＬＢ法により形成するポリイミド膜からなる水平配向膜を、ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を制御して単位面積当たりに長鎖アルキル基が所定の割合で残留するように形成したものであり、前記長鎖アルキル基は疎水性をもっているため、水平配向膜の単位面積当たりの長鎖アルキル基の残留割合を多くするほど、配向膜の表面張力が小さくなり、液晶分子が、前記表面張力に応じたプレチルト角をもって水平配向する。

【００１５】このため、前記ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を制御して、上記水平配向膜の単位面積当たりの長鎖アルキル基の残留割合を制御すれば、液晶分子を所望のプレチルト角をもたせて配向させて、液晶の初期配向不良や駆動電圧印加時のリバースチルトディスクリネーション配向不良等がない良好な表示品質を得ることができる。

【００１６】また、本発明の水平配向膜の形成方法は、ＬＢ法によりポリアミック酸と長鎖アルキル基を有するアミンとを反応させてなる化合物の単分子膜を積層し、この単分子膜の積層膜をイミド化処理して長鎖アルキルアミンが残留するポリイミド膜を形成するものであり、前記ポリアミック酸と長鎖アルキル基を有するアミンとの混合比を、あらかじめ設定した単分子膜の積層数とそのイミド化条件とに応じて制御することにより、それに応じて前記ポリイミド膜の長鎖アルキル基残留割合が決まるため、液晶分子を所望のプレチルト角をもたせて配向させる水平配向膜を得ることができる。

【００１７】

【実施例】以下、本発明の実施例を図面を参照して説明する。

【００１８】図１は液晶表示素子の断面図である。この液晶表示素子は、ガラス等からなる一対の透明基板１，２を枠状のシール材３を介して接合し、この両基板１，２間のシール材３で囲まれた領域に液晶を封入したもの

で、両基板１，２の互いに対向する面にはそれぞれ、透明電極４，５が形成されている。また、この両基板１，２の電極形成面は、酸化硅素（Ｓｉ Ｏ$_2$）等からなる透明な絶縁膜６，７で覆われており、この絶縁膜６，７の上に水平配向膜８，９が形成されている。

【００１９】なお、この液晶表示素子は、ＴＮモードまたはＳＴＮモードのものであり、両基板１，２間に封入された液晶の分子Ａは、両基板１，２側の配向膜８，９の近傍の液晶分子Ａの各配向方向を前記配向膜８，９で規制され、両基板１，２間において所定のツイスト角でツイスト配向している。ただし、図１では、便宜上、液晶分子Ａをツイスト配向していない状態で示している。

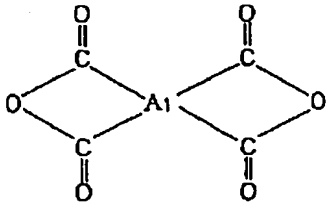
【００２０】上記水平配向膜８，９は、いずれも、ポリアミック酸と長鎖アルキル基を有するアミン（以下、長鎖アルキルアミンという）とを反応させてなる化合物の単分子膜を数層～数十層に重ねて被着させた膜をイミド化したポリイミド膜からなっている。

【００２１】この水平配向膜８，９は、次のような方法で形成する。なお、ここでは、一方の基板１に設ける水平配向膜８の形成について説明するが、他方の基板２に設ける水平配向膜９も同様にして形成する。

【００２２】上記ポリアミック酸は、下記の［化３］の構造式で表わされ、このポリアミック酸は、［化１］の構造式で表わされるテトラカルボン酸二無水物と、［化２］の構造式で表わされるジアミンとを合成して得られる。

【００２３】

【化１】



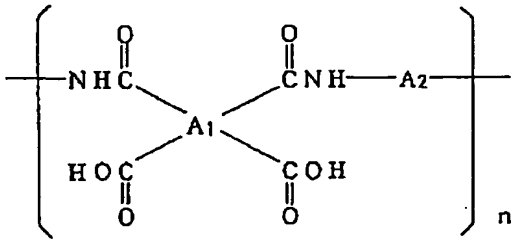
【００２４】

【化２】

$$H_2N—A_2—NH_2$$

【００２５】

【化３】



nは１以上の整数

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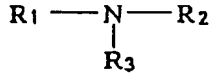
【００２６】また、上記長鎖アルキルアミンは、親水性をもつポリアミック酸に疎水性を付与するためのものであり、この長鎖アルキルアミンは次の［化４］の構造式で表わされる。

【００２７】

【化４】



R_1，R_2 は低級アルキル基または水素原子

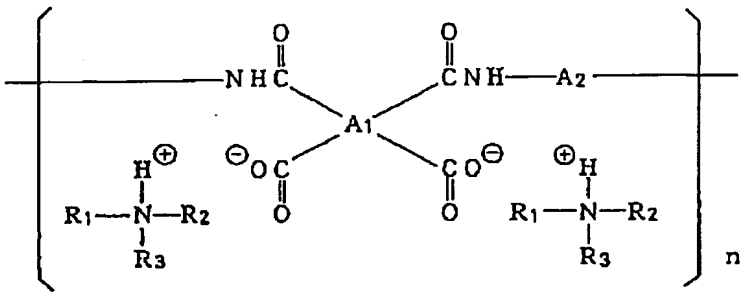
R_3 は長鎖のアルキル基

6

【００２８】上記ポリアミック酸を溶媒に溶かした溶液と、上記長鎖アルキルアミンを同じ溶媒に溶かした溶液とを所定の割合で混合し、ポリアミック酸と長鎖アルキルアミンとをイオン結合反応させて、下記の［化５］の構造式で表わされるポリアミック酸誘導体化合物（ポリアミック酸塩）の溶液を作成する。なお、上記ポリアミック酸および長鎖アルキルアミンの溶媒としては、ＮＭＰ（Ｎ－メチル－２－ピロリジノン）とベンゼンを１：１の割合で混合した混合溶媒を用いる。

【００２９】

【化５】



【００３０】そして、上記水平配向膜８は、透明電極４を形成しその上に絶縁膜６を形成した基板１上に、ＬＢ法によって上記ポリアミック酸誘導体化合物の単分子膜を所定層に積層し、この単分子膜の積層膜を熱処理することにより形成される。図２は、基板１上にポリアミック酸誘導体化合物の単分子膜をＬＢ法によって被着させる方法を示している。この単分子膜の被着は次のようにして行なう。まず、上記基板１の単分子膜被着面（絶縁膜６面）に親水性処理を施し、この基板１を水槽１０内の水中に垂直に浸漬させる。

【００３１】次に、水面高さに設けたバー状の移動バリア１１と基板１との間の水面上に上記ポリアミック酸誘導体化合物の溶液を滴下して、その単分子膜ａを水面上に展開させる。

【００３２】次に、移動バリア１１を基板方向に移動させて水面上の単分子を密集させ、単分子膜ａの表面圧を一定圧（２５dyn/cm）に調整した後、移動バリア１１を基板方向に一定速度（２mm/min）で移動させて単分子膜ａを基板方向に押しながら、これに同調させて基板１を引上げて、水面上の単分子膜ａを基板１上に被着させる。

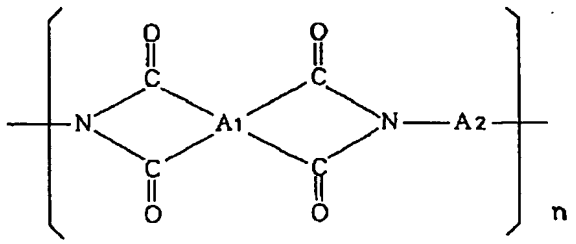
【００３３】このとき、水面上の単分子は、親水性をもつ部分が親水性処理を施してある基板１に付着して引上げられるため、単分子膜ａは、分子がほぼ一方向に並んだ状態で基板１上に被着する。以下は、上記単分子膜ａの被着工程を繰返して、基板１上に上記単分子膜ａを所定層に積層する。

【００３４】このようにして基板１上にポリアミック酸誘導体化合物の単分子膜ａを積層した後は、２００℃以上で約１時間加熱する熱処理を行なう。この熱処理により、基板１上の積層膜のイミド化が進み、アルキルアミンが残留する水平配向膜８が形成される。

【００３５】この場合、ポリアミック酸と長鎖アルキルアミンとがイオン結合した化合物であるポリアミック酸誘導体化合物の単分子積層膜は、そのアルキルアミンが除去されるとともに脱水閉環され、次の［化６］のような構造をもったポリイミドとなるようにイミド化されるが、そのイミド化が完結されずに、アルキルアミンが所定の割合で残留する。このアルキルアミンの残留量は、熱処理条件等を一定にした場合、ポリアミック酸と長鎖アルキルアミンとの混合比によって変化する。したがって、ポリアミック酸と長鎖アルキルアミンとの混合比を適宜設定することによって長鎖アルキル基の残留割合を制御することができる。

【００３６】

【化６】



【００３７】そして、上記液晶表示素子においては、その両基板１，２のポリイミド膜からなる水平配向膜８，９が、ポリアミック酸と長鎖アルキルアミンとの混合比を適宜設定することにより、その単位面積当たりの上記［化４］に示した長鎖アルキルアミンにおける長鎖アル

キル基R，の残留割合を制御して形成され、この水平配向膜８，９により液晶分子Ａを所望のプレチルト角φをもって配向させている。

【００３８】図３および図４は、ポリアミック酸と長鎖アルキルアミンとの混合比を制御してＬＢ法により形成したポリイミド膜からなる水平配向膜８，９の長鎖アルキル基R，の残留状態を模式的に示す図であり、図３はポリアミック酸と長鎖アルキルアミンの量（モル量）をほぼ同じにしたときの長鎖アルキル基残留状態、図４はポリアミック酸の量よりも長鎖アルキルアミンの量を多くしたときの長鎖アルキル基残留状態を示している。

【００３９】この図３および図４のように、上記ＬＢ法により形成したポリイミド膜からなる水平配向膜８，９の長鎖アルキル基R，の残留割合は、ポリアミック酸と長鎖アルキルアミンとの混合比によって変化し、また長鎖アルキルアミンの量を多くするほど、長鎖アルキル基R，の残留割合が増加するとともに、その分布も均一になる。

【００４０】そして、上記液晶表示素子においては、ＬＢ法により形成するポリイミド膜からなる水平配向膜８，９を、その単位面積当たりに長鎖アルキル基R，が所定の割合で残留するようにポリアミック酸と長鎖アルキルアミンとの混合比を制御して形成しているため、液晶分子を所望のプレチルト角φをもたせて配向させることができる。

【００４１】これは、上記長鎖アルキル基が疎水性をもっているためであり、水平配向膜８，９の単位面積当たりの長鎖アルキル基R，の残留割合を多くするほど、配向膜８，９の表面張力が小さくなり、液晶分子Ａがプレチルト角φをもって配向する。

【００４２】このため、上記ポリアミック酸と長鎖アルキルアミンとの混合比を制御して、水平配向膜８，９の単位面積当たりの長鎖アルキル基R，の残留割合を制御すれば、液晶分子Ａを所望のプレチルト角をもたせて配向させて、液晶の初期配向不良や駆動電圧印加時のリバースチルトディスクリネーション配向不良等がない良好な表示品質を得ることができる。

【００４３】上記のような長鎖アルキル基残留割合の水平配向膜８，９は、ポリアミック酸と長鎖アルキルアミンとの混合比を、上述したＬＢ法により積層する単分子膜ａの積層数とそのイミド化条件とに応じて制御して形成する。

【００４４】すなわち、この水平配向膜８，９の形成方法は、ＬＢ法によりポリアミック酸と長鎖アルキルアミンとを反応させてなる化合物の単分子膜ａを積層する際に、前記ポリアミック酸と長鎖アルキルアミンとの混合比を制御することにより、前記単分子膜ａの積層膜をイミド化処理して形成するポリイミド膜における長鎖アルキル基R，の残留割合を制御するものであり、前記ポリアミック酸と長鎖アルキルアミンとの混合比を単分子膜ａの積層数とそのイミド化条件とに応じて制御すると、それに応じて単位面積当たりの長鎖アルキル基残留割合が決まるため、液晶分子Ａを所望のプレチルト角φをもたせて配向させる水平配向膜８，９を得ることができる。

【００４５】図５は、上記ポリアミック酸と長鎖アルキルアミンとの混合比と、上記単分子膜ａの積層数と、イミド化温度と、形成された配向膜の表面張力との関係を示しており、ここでは、ポリアミック酸と長鎖アルキルアミンとの混合比（モル比）を、ポリアミック酸：長鎖アルキルアミン＝１：３と、ポリアミック酸：長鎖アルキルアミン＝１：５との二通りに選び、それぞれをイミド化温度２００℃でイミド化処理した例を示している。

【００４６】この図５のように、ポリアミック酸と長鎖アルキルアミンとの混合比を１：３にして形成したポリイミド膜からなる配向膜は、単分子膜ａの積層数が１８層程度以下の場合は表面張力が大きすぎて液晶分子Ａをほとんどプレチルトさせず（プレチルト角φ＝０）、それよりも単分子膜ａの積層数を多くした場合に、液晶分子Ａをある程度のプレチルト角φ（例えば積層数が２３層の場合でφ＝３．２°）をもって配向させる表面張力になる。なお、この表面張力は、単分子膜ａの積層数を多くするほど小さくなり、それにともなって液晶分子Ａのプレチルト角φが大きくなる。

【００４７】また、ポリアミック酸と長鎖アルキルアミンとの混合比を１：５にして形成したポリイミド膜からなる配向膜は、単分子膜ａの積層数が１０層程度以下の場合は表面張力が大きすぎて液晶分子Ａがほとんどプレチルトしないが、それよりも単分子膜ａの積層数を多くすると、液晶分子Ａがプレチルト角φをもって配向する表面張力になる。この場合のプレチルト角φは、例えば積層数が約１１層の場合でφ＝０．４°、積層数が約１７層以上の場合でφ＝１３°以上である。なお、この場合も、配向膜の表面張力は単分子膜ａの積層数を多くするほど小さくなり、それにともなって液晶分子Ａのプレチルト角φが大きくなるが、積層数が約２２層を越えると、プレチルト角φが９０°に近くなって、液晶分子Ａが垂直配向してしまう。

【００４８】なお、ポリアミック酸に対する長鎖アルキルアミンの量が３倍（混合比１：３）以下であっても、単分子膜ａの積層数をさらに多くすることによって液晶分子Ａのプレチルト配向させることができるが、単分子膜ａの積層数を多くすると、配向膜８，９が厚くなって、印加電圧が配向膜において大きく降下する。

【００４９】したがって、上記ポリアミック酸と長鎖アルキルアミンとの混合比は、ポリアミック酸：長鎖アルキルアミン＝１：３～１：５の範囲とするのが望ましく、この範囲であれば、単分子膜ａの積層数をあまり多くすることなく、液晶分子Ａを所望のプレチルト角φをもたせて配向させる水平配向膜８，９を得ることができ

る。

【００５０】なお、上記実施例では、単分子膜ａの積層膜のイミド化処理を熱処理によって行なっているが、このイミド化処理は、酸無水物等の溶液による化学処理によっても、また前記化学処理と上記熱処理との両方を併用して行なってもよく、その場合も、ポリアミック酸と長鎖アルキルアミンとの混合比を単分子膜ａの積層数とそのイミド化条件とに応じて制御すれば、液晶分子を所望のプレチルト角をもたせて配向させる水平配向膜を得ることができる。

【００５１】また、上記実施例の液晶表示素子は、ＴＮモードまたはＳＴＮモードのものであるが、本発明は、ＥＣＢ（電界制御型複屈折）モードのうちの水平配向型の液晶表示素子や、強誘電性液晶または反強誘電性液晶を用いた液晶表示素子等にも適用することができる。

【００５２】

【発明の効果】本発明の液晶表示素子は、ＬＢ法により形成するポリイミド膜からなる水平配向膜を、ポリアミック酸と長鎖アルキルアミンとの混合比を制御して単位面積当たりに長鎖アルキル基が所定の割合で残留するように形成したものであるから、液晶分子を所望のプレチルト角をもたせて配向させて、液晶の初期配向不良や駆動電圧印加時のリバースチルトディスクリネーション配向不良等がない良好な表示品質を得ることができる。

【００５３】また、本発明の水平配向膜の形成方法は、ＬＢ法によりポリアミック酸と長鎖アルキルアミンとを反応させてなる化合物の単分子膜を積層し、この積層膜をイミド化して長鎖アルキル基が残留するポリイミド膜

を形成する方法で、前記ポリアミック酸と長鎖アルキルアミンとの混合比をあらかじめ設定した単分子膜の積層数とそのイミド化条件とに応じて制御することにより、前記ポリイミド膜の長鎖アルキル基の残留割合を制御するものであるため、液晶分子を所望のプレチルト角をもたせて配向させる水平配向膜を得ることができる。

【図面の簡単な説明】

【図１】本発明の一実施例を示す液晶表示素子の断面図。

【図２】ＬＢ法による基板上への単分子膜の積層法を示す図。

【図３】ポリアミック酸と長鎖アルキルアミンの量をほぼ同じにして形成した水平配向膜の長鎖アルキル基Ｒ₁の残留状態を模式的に示す図。

【図４】ポリアミック酸の量よりも長鎖アルキルアミンの量を多くして形成した水平配向膜の長鎖アルキル基Ｒ₁の残留状態を模式的に示す図。

【図５】ポリアミック酸と長鎖アルキルアミンとの混合比と、単分子膜の積層数と、イミド化温度と、形成された配向膜の表面張力との関係を示す図。

【符号の説明】

１，２…基板

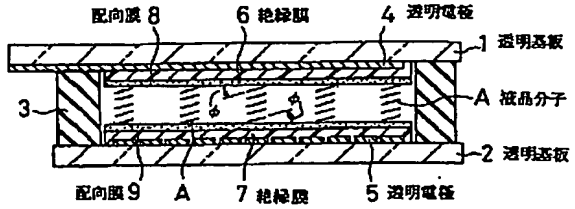
４，５…電極

６，７…絶縁膜

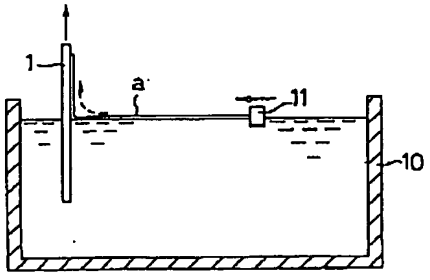
８，９…ＬＢ法により形成したポリイミド膜からなる水平配向膜

Ａ…液晶分子

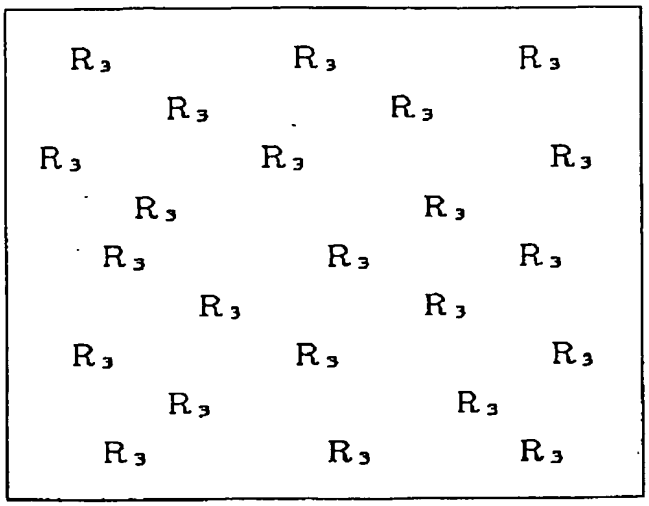
【図１】



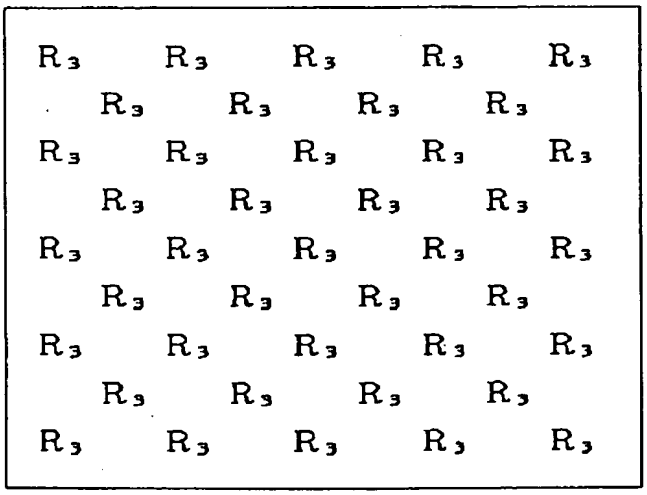
【図２】



【図３】



【図４】



【図５】